Optical Dispersion: An Analysis of its Actual Dependence upon Physical Conditions.

By T. H. Havelock, M.A., D.Sc., Armstrong College, Newcastle-on-Tyne.

(Communicated by Prof. Sir Joseph Larmor, Sec. R.S. Received October 10,—Read November 24, 1910.)

CONTENTS.

		PAGE
1.	Introduction	492
2.	Refractive Index and Physical State	494
3.	Temperature Variation: Organic Liquids	496
4.	Carbon Disulphide and Water	497
5.	Organic Liquids (Falk)	500
6.	Variation under Pressure	502
7.	Artificial Double Refraction in Liquids	502
8.	Temperature Variation in Solids	505
9.	Change from Vapour to Liquid	508
10.	Absolute Values of the Variable σ	509
11.	Dispersion Formulæ: Absorption Maxima	512
12.	Displacement of Absorption Maxima by Pressure and Heat	517
13.	Summary	522

1. *Introduction.*

The influence of a transparent medium upon light passing through it may be ascribed to two factors; one is the existence, in each individual molecule or particle, of vibrating parts with certain natural frequencies, and the other is the physical condition of the aggregation of molecules composing the medium. Suppose that a typical vibrating part is an electrified particle of charge e and mass m, whose free vibrations are given by equations of the type

$$m\frac{d^2x}{dt^2}+fx = 0. \tag{1}$$

Let X be the corresponding component of electric force in the incident light wave. The impressed force, to be supplied on the right-hand side of (1) for the actual motion, is not simply eX, but has an additional term to express the effect of the surrounding molecules; the simplest conception of this effect indicates a term directly proportional to the average polarisation P of the surrounding molecules at each instant. Hence, instead of (1), we have an equation

$$m\frac{d^2x}{dt^2}+fx = e\,(\mathrm{X}+\sigma\mathrm{P}_x). \tag{2}$$

As regards the numerical value of the co-efficient σ, little can be said beforehand on theoretical grounds; certain considerations, given in the present connection by Lorentz and by Larmor, indicate that for gases and liquids σ should be approximately $\frac{1}{3}$.

The following investigation is an attempt to extract from available experimental data, information about the numerical value of σ and its variation with changing physical conditions. The problems concerned are those of optical dispersion in isotropic and œolotropic media, and the changes produced by varying density, pressure and temperature, or by the action of external electric or magnetic fields. No attempt is made to explain the intimate mechanism of these phenomena, that is, the physical process by which the value of σ is altered; rather, the term is used as a possible means for including the various effects under one formal scheme, at least for a first approximation. The method is, in fact, analogous to the usual procedure of describing absorption effects by introducing a term in dx/dt into equation (2), without thereby specifying completely the physical process involved in absorption.

If we ignore the effect of surrounding molecules in equation (2), that is, if we put σ zero, the dispersion formula which can be deduced is of the type

$$n^2-1 = \Sigma_s \frac{C_s}{\lambda^2-\lambda_s{}^2}, \tag{3}$$

where n is the refractive index of the medium for wave-length λ, C_s is a constant associated with the vibrating electrons of type s, and is proportional to the number of such per unit volume, λ_s is the wave-length corresponding to the natural frequency of the same type, and the summation Σ extends over all the types. Again, if we put σ equal to $\frac{1}{3}$, we obtain a dispersion formula

$$\frac{n^2-1}{n^2+2} = \Sigma_s \frac{C_s}{\lambda^2-\lambda_s{}^2}. \tag{4}$$

In both cases, if we assume the quantities C_s to be proportional to the density ρ, and divide either of equations (3) and (4) by ρ, we obtain on the right-hand side a quantity dependent only upon the constitution of the individual molecule; the expression on the other side must also be independent of the physical conditions of the aggregation. In this way two relations connecting refractive index and density have arisen, namely

$$\frac{n^2-1}{\rho} = \text{constant}; \qquad \frac{n^2-1}{n^2+2}\frac{1}{\rho} = \text{constant}. \tag{5}$$

These relations have been the subject of numerous investigations. The second one gives generally a better agreement with the facts, especially in cases of change of state from vapour to liquid; however, when the refractive indices at different temperatures and under different pressures are compared, it is found that neither relation expresses all the facts; these cannot be ascribed merely to change of density.

We might then fall back upon simply asserting that the quantities C_s and λ_s in (3) or (4) must vary with the physical conditions, or, in other words, the natural frequencies of the individual molecules must be affected by pressure, temperature, or external action on the medium; for a small variation one would obtain from (3) a dispersion formula

$$2n\,dn = \Sigma_s \left\{ \frac{dC_s}{\lambda^2-\lambda_s^2} + \frac{2C_s\lambda_s d\lambda_s}{(\lambda^2-\lambda_s^2)^2} \right\}. \tag{5}$$

This in fact has generally been the procedure in previous investigations. In contrast to this method, we shall consider here to what extent the facts can be expressed in terms of two variables, the density ρ and the quantity σ, without introducing changes in the inherent molecular frequencies.

It has been remarked that the cause of the disagreement between the second relation in (5) and experiment must be looked for partly in the fact that σ is not exactly equal to $\frac{1}{3}$, partly also in changes that take place in the interior of the particles when a body is heated or compressed; these changes causing a variation in the value of the coefficients f in equation (2).* Without denying that both these are probably true contributing causes, it seems of interest to examine separately the former supposition, especially as it has been ignored in favour of the latter as sole cause.

2. *Refractive Index and Physical Conditions.*

If we retain the quantity σ we can deduce a dispersion formula like (4) but with $(n^2-1)/\{1+\sigma(n^2-1)\}$ on the left hand side. The coefficients C_s are proportional to the number of vibrating parts of given type in unit volume; if we make the usual assumption that they are proportional to the density and if we divide through by ρ, we have

$$\frac{n^2-1}{1+\sigma(n^2-1)}\frac{1}{\rho} = \Sigma \frac{C_s}{\lambda^2-\lambda_s^2}. \tag{6}$$

On the right hand we have now, by supposition, a function of the wave-length λ and the constitution of the individual particle; hence for a given wave-length and for all physical conditions of the aggregation of particles, we should have

$$\frac{n^2-1}{1+\sigma(n^2-1)}\frac{1}{\rho} = \text{const.} \tag{7}$$

---

* H. A. Lorentz, 'The Theory of Electrons,' p. 147.

It may be noted that if we divide throughout by σ we may write this relation as

$$\frac{n^2-1}{n^2+a}\frac{1}{\rho} = \text{const.} \tag{8}$$

This has been used as a generalised form of (5); but it clearly ignores the dependence of σ upon the physical conditions, and has in fact been no more successful than the simpler relation.

The formula in (7) may be put more conveniently as

$$\rho\left(\sigma+\frac{1}{n^2-1}\right) = \text{const.} \tag{9}$$

Now we have no means of calculating σ independently, so this relation cannot be verified directly. To obtain numerical values of σ we shall have to fix its value in some standard condition; before doing so, we can deduce a difference-equation which can be put to the test of experiment. If the suffixes 1 and 2 denote values in two different states of a medium composed of similar individual particles we have

$$\rho_1\left(\sigma_1+\frac{1}{n_1{}^2-1}\right) = \rho_2\left(\sigma_2+\frac{1}{n_2{}^2-1}\right).$$

Hence $$\frac{\rho_2}{n_2{}^2-1}-\frac{\rho_1}{n_1{}^2-1} = \rho_1\sigma_1-\rho_2\sigma_2 = \text{C}. \tag{10}$$

Thus, for two physical states, the difference in $\rho/(n^2-1)$ is constant for all wave-lengths; by supposition σ is independent of the wave-length, hence the left-hand side of (10) is a function only of physical conditions such as temperature, pressure, density, and so forth. The two relations given previously in (5) are special cases of (10) given by $\sigma_1 = \sigma_2 = 0$ and $\sigma_1 = \sigma_2 = \frac{1}{3}$; so that if either of the formulæ (5) held, the constant in (10) would have the value zero or $\frac{1}{3}(\rho_1-\rho_2)$ respectively.

Two special forms of (10) for small changes should be noted, that is, when it may be written $d\{\rho/(n^2-1)\} = \text{constant}$.

First, if the pressure is constant and the temperature t is the independent variable, we have

$$\frac{\alpha}{n^2-1}+\frac{2n}{(n^2-1)^2}\frac{dn}{dt} = \text{const.}, \tag{11}$$

where $\alpha = -d(\log\rho)/dt$ = coefficient of cubical expansion.

Secondly, if the temperature is constant and the pressure p varies,

$$\frac{\beta}{n^2-1}-\frac{2n}{(n^2-1)^2}\frac{dn}{dp} = \text{const.}, \tag{12}$$

where $\beta = d(\log\rho)/dp$ = coefficient of compressibility.

From (11) we have

$$\frac{dn}{dt} = C_1 \frac{(n^2-1)^2}{2n} - \alpha \frac{n^2-1}{2n}. \tag{13}$$

Thus if C_1 is a positive quantity it is possible for the temperature variation dn/dt to change sign from positive to negative; this would occur for a wave-length at which the index of refraction equals $\sqrt{(1+\alpha/C_1)}$.

We shall examine now the relations (10), (11), and (12). Where special reference is not made, the data used have been taken from Landolt and Börnstein ('Physikalisch-Chemische Tabellen') or from Winkelmann ('Handbuch der Physik').

3. *Temperature Variation: Organic Liquids.*

A preliminary comparison may be made by using a set of liquid organic compounds which have been examined in a similar manner by Voigt*; the data are taken from the collection in his paper. Voigt adopts the hypothesis that thermal or mechanical deformation produces a change in the natural frequencies of the vibrations within the molecule in addition to the effect due merely to the change of density; he gives expression to this change by tabulating for different wave-lengths the values of a quantity T defined by

$$\frac{n_1^2-1}{\rho_1} - \frac{n_2^2-1}{\rho_2} = \frac{(\rho_1-\rho_2)\,T}{\rho_1\rho_2}. \tag{14}$$

Apart from a few exceptions, due probably to inaccurate data, Voigt finds that for liquids T is positive and increases regularly with decreasing wave-length. Now if we compare (14) with (10) we see that C is equal to $T(\rho_1-\rho_2)/(n_1^2-1)(n_2^2-1)$; it is possible then for C to remain constant for different wave-lengths since, in general, n_1 and n_2 increase with decreasing wave-length.

Table I shows the results of the calculations for the heat expansion of nine liquids, namely, those used by Voigt as a random selection from available data; in each case the mean value of C, that is of $\rho_2/(n_2^2-1)-\rho_1/(n_1^2-1)$, is compared with the value of $\frac{1}{3}(\rho_1-\rho_2)$, so that one sees the divergence from the simpler Lorentz formula.

One may say that the general result of these calculations is favourable to the relation given in (10); such divergences as occur are irregular in character, and are probably due in these cases to insufficient accuracy of the values of density and refractive index. Without laying too much stress on the actual numerical values, it appears that C may be considered constant within the range of wave-lengths concerned in each case.

---

* W. Voigt, 'Annalen der Physik' (4), 1901, vol. 6, p. 459.

More recent experiments are available in the case of water and carbon disulphide and we shall examine these now.

Table I.

Aniline.—12°—28°. Mean C = 0·00280; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·00455.

λ.........	691	656	589	486	434
10^5 C.........	256	294	269	289	290

Acetylene dibromide.—15°—25°. Mean C = 0·00516; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·00750.

λ.........	656	589	486	397
10^5 C.........	517	525	518	502

Ethyl alcohol.—0°—20°. Mean C = 0·00410; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·00563.

λ.........	656	589	486	397
10^5 C.........	413	406	407	415

Ethylene bromide.—15°—25°. Mean C = 0·00534; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·00758.

λ.........	656	589	486	397
10^5 C.........	536	533	524	543

Benzene.—12°—28°. Mean C = 0·00425; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·00545

λ.........	691	656	589	486	434
10^5 C.........	428	412	481	395	409

Iodobenzene.—7°—22·2°. Mean C = 0·00224; $\frac{1}{3}(\rho_2-\rho_2)$ 0·00790.

λ.........	760	589	486	397
10^5 C.........	268	294	203	129

Methylaconate.—16°—24°. Mean C = 0·00058; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·00319.

λ.........	656	589	486	434
10^5 C.........	57	55	60	61

Thiophene.—16°—24°. Mean = 0·0004; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·0033.

λ.........	656	589	486	434
10^5 C.........	34	56	45	24

Vinyl tribromide.—15°—25°. Mean C = 0·00479; $\frac{1}{3}(\rho_1-\rho_2)$ = 0·00733.

λ.........	656	589	486	434
10^5 C.........	470	471	476	500

4. *Carbon Disulphide and Water.*

Flatow* has examined in detail the dispersion of water and carbon disulphide, measuring the absolute refractive index at various wave-lengths, and for several different temperatures; he concludes that the Lorentz relation $(n^2-1)/(n^2+2)\rho$ = const. is approximately satisfied, and he has also calculated for each temperature a dispersion formula of the type

$$n^2 = m+\frac{m'\lambda^2}{\lambda^2-\lambda'^2}-k\lambda^2,$$

in order to study the variation of λ' with the temperature. We shall consider dispersion formulæ in a later section; at present we use Flatow's experimental results to test the relation (10).

---

* E. Flatow, 'Annalen der Physik' (4), 1903, vol. 12, p. 85.

Carbon disulphide.—We have measurements of n at nine wave-lengths for the temperatures -10°, 0°, 20°, and 40°. The densities have been calculated from the known expansion of CS_2, and with the value $\rho_0 = 1{\cdot}2931$. We are able in this way to form three sets of differences; using the notation

$$C_0^{20} = \left(\frac{\rho}{n^2-1}\right)_{20^\circ} - \left(\frac{\rho}{n^2-1}\right)_{0^\circ},$$

the results are shown in Table II.

Table II.—Carbon Disulphide.

λ.	$10^5\,C_0^{-10}$.	$10^5\,C_0^{20}$.	$10^5\,C_{20}^{40}$.
274	327	676	657
361	310	583	639
394	288	595	668
441	266	594	678
467	263	598	635
480	253	593	642
508	253	604	635
533	256	609	645
589	274	617	639

Comparing mean values of C and the changes in density, we have the following:—

$$C_0^{-10} = 0{\cdot}00274; \quad C_0^{20} = 0{\cdot}00607; \quad C_{20}^{40} = 0{\cdot}00649;$$

$$\tfrac{1}{3}(\rho_{-10}-\rho_0) = 0{\cdot}0049; \quad \tfrac{1}{3}(\rho_0-\rho_{20}) = 0{\cdot}0099; \quad \tfrac{1}{3}(\rho_{20}-\rho_{40}) = 0{\cdot}0103.$$

As regards the constancy of C, the results may be regarded as satisfactory, considering the order of accuracy that may be expected. Considerable deviations occur at the two smaller wave-lengths ($0{\cdot}274\,\mu$ and $0{\cdot}361\,\mu$). It must be remembered that here we approach the dominating region of absorption in the ultra-violet, which is in the neighbourhood of $0{\cdot}225\,\mu$; and it is known that also a minor region of absorption occurs between these two values, near $0{\cdot}325\,\mu$, which is sufficient to cause slight anomalies in the refractive index.* In the relation (10) absorption has not been taken directly into account, so deviations may be expected as one approaches a region of absorption.

---

* W. Fricke, 'Annalen der Physik,' 1905, vol. 16, p. 865.

Another way of expressing these results is by using the alternative form (11), the changes being small and the pressure constant; thus approximately

$$C_0^{20} = 20\,\frac{d}{dt}\left(\frac{\rho}{n^2-1}\right)_{10^\circ}, \qquad \frac{C_0^{20}}{20\rho_{10}} = -\frac{\alpha}{n^2-1} - \frac{2n}{(n^2-1)^2}\frac{dn}{dt}.$$

Using the mean value of C_0^{20} we find the rate of change of n at 10° given by

$$\frac{dn}{dt} = -0{\cdot}001162\,\frac{(n^2-1)}{2n} - 0{\cdot}000238\,\frac{(n^2-1)^2}{2n}. \qquad (15)$$

In this case we notice that dn/dt remains negative for all wave-lengths. Graphing dn/dt with respect to λ from (15) we obtain practically the same curve as that given by Flatow as the result of his experiments; in the visible region dn/dt varies only slowly, but in the ultra-violet it diminishes very rapidly algebraically with decreasing wave-length. As regards variation with the temperature, it should be noted that both the numerical coefficients in (15) would be slightly different for other temperatures.

Water.—We have observations at five temperatures, 0°, 20°, 40°, 60°, and 80°; using the same range of wave-lengths, and with the same notation, we have the results in Table III.

Table III.—Water.

λ.	$10^5\,C_0^{20}$.	$10^5\,C_{20}^{40}$.	$10^5\,C_{40}^{60}$.	$10^5\,C_{60}^{80}$.
274	191	233	310	313
308	188	252	343	350
340	190	261	363	369
361	198	259	366	378
394	188	276	377	385
441	186	282	385	400
480	170	264	384	410
533	165	268	385	404
589	159	267	400	394

From these we have for mean values and difference of densities:

$$C_0^{20} = 0{\cdot}00181; \qquad C_{20}^{40} = 0{\cdot}00263;$$

$$\tfrac{1}{3}(\rho_0-\rho_{20}) = 0{\cdot}00055; \qquad \tfrac{1}{3}(\rho_{20}-\rho_{40}) = 0{\cdot}00230;$$

$$C_{40}^{60} = 0{\cdot}00368; \qquad C_{60}^{80} = 0{\cdot}00378;$$

$$\tfrac{1}{3}(\rho_{40}-\rho_{60}) = 0{\cdot}00301; \qquad \tfrac{1}{3}(\rho_{60}-\rho_{80}) = 0{\cdot}00380.$$

It cannot be said that the results are very satisfactory when analysed in this manner. On the other hand there is nothing decisive against the present theory; for if C_0^{20} has a slight regular decrease, C_{40}^{60} and C_{60}^{80} increase a little with increasing wave-length, while C_{20}^{40} is irregular. Further, if we make the calculations for the smallest wave-length used ($0{\cdot}214\,\mu$), we find small values for the four quantities, viz., $C_0^{20} = 0{\cdot}00148$; $C_{20}^{40} = 0{\cdot}00150$; $C_{40}^{60} = 0{\cdot}00216$; $C_{60}^{80} = 0{\cdot}00185$. Flatow himself, in calculating dispersion formulæ, found greater deviations for wave-lengths between $0{\cdot}217$ and $0{\cdot}267\,\mu$; owing to these appearing at all the temperatures, he concludes that they are not due to experimental inaccuracies, but possibly to a neglected region of absorption.

Another point in which water is peculiar in the present connection is the occurrence of a minimum density in the region considered; as regards the constancy of $(n^2-1)/(n^2+2)\rho$, we see from the comparison of C_0^{20} and $\frac{1}{3}(\rho_0 - \rho_{20})$ that this fact makes a considerable divergence in this region.

Taking the observations and calculations for water as they stand, one concludes that, although the results allow of the present interpretation, the evidence is more doubtful in character than for other substances examined.

5. *Organic Liquids.*

Falk* has investigated in great detail the variation of refractive index with temperature for a series of liquid organic compounds, using the sodium line (D_1) and the three hydrogen lines (C, F, and G′); the density of each liquid was also determined at various temperatures. It was found that within the limits of experimental error, both the refractive index for given wave-length and the density were linear functions of the temperature. For five temperatures ranging from 10° to 80°, Falk calculated, for the four wave-lengths, the quantities $(n-1)/\rho$, $(n^2-1)/\rho$, and $(n^2-1)/(n^2+2)\rho$; each of these quantities shows for a given wave-length a small, but regular and continuous, change with the temperature, either increase or decrease. The quantity a was also calculated, so as to give the best average results for the relation $(n^2-1)/(n^2+a)\rho$ = constant, for each liquid. For the present purpose, the data for the two extreme temperatures, 10° and 80°, have been used to calculate C_{10}^{80}, the difference in value of $\rho/(n^2-1)$ for the two temperatures for each wave-length; the results are shown in Table IV.

The only substances which show regular variation in the values of C_{10}^{80} are nitrobenzene and monomethylaniline. It is stated that owing to the colour of the liquid the G′ line (434) was too indistinct for measurements

---

* K. G. Falk, 'Journ. Amer. Chem. Soc.,' 1909, vol. 31, p. 86 and p. 806.

Table IV.—Values of $10^4\,C_{10}^{80}$.

Wave-length	656.	589.	486.	434.	Mean.	$\frac{1}{3}(\rho_{10}-\rho_{80})\,.\,10^4$.
Diisoamyl	112	113	116	107	112	180
Dimethylaniline	110	107	109	112	109	193
n-Heptyl alcohol	104	90	107	101	100	166
Benzyl alcohol	138	130	134	133	134	175
n-Butyric acid	104	90	88	90	93	230
Acetylacetone	282	288	315	302	297	223
Isobutyl acetate	137	129	136	140	136	246
Ethyl *n*-butyrate	141	140	130	136	137	250
Isoamyl acetate	141	130	134	126	133	228
Methylhexyl ketone	97	95	90	96	94	200
Nitrobenzene	122	127	128	—	126	230
Monomethylaniline	105	107	126	—	113	189
Benzyl cyanide	93	94	94	93	94	190
Benzaldehyde	99	92	95	104	98	207

to be made in these two cases; thus the regular increase seems clearly to be connected with exceptional absorption. For all the other substances it can at least be said that there is no regular increase or decrease of C with decreasing wave-length, so that it is permissible to regard the variations as accidental. In the previous section we noticed that Voigt has measured the effect of temperature by the change in $(n^2-1)/\rho$, and found that this change increased regularly with decreasing wave-length in general. The same remark applies to the present collection of liquids, with one or two doubtful cases; however, in about six cases the regular increase is broken by the quantity being greater for the C line than for the D line. The effect of this can be noticed in the column (656) in the table above. For instance, if we calculate the difference in value of $(n^2-1)/\rho$ at 10° and 80° for benzyl alcohol for the four wave-lengths, we obtain the sequence 0·0229, 0·0220, 0·0240, and 0·0251. This might possibly indicate some experimental error for observations with the C line; if not, it seems a curious effect. The mean values in column 5 of Table IV are equal to the mean values of $\sigma_{10}\rho_{10}-\sigma_{80}\rho_{80}$, from relation (10). We cannot as yet calculate absolute values for σ, but the numbers C_{10}^{80} measure the rate of increase of $\sigma\rho$ with temperature. The large value of 0·0297 for acetyl acetone may be noticed; according to Falk, this substance is exceptional in the above collection, owing to its being a tautomeric mixture of two forms, the relative proportions changing with the temperature. Another point is that the isomeric substances, isobutyl acetate and ethyl *n*-butyrate have practically the same rate of change for the product $\sigma\rho$.

6. *Pressure Variation.*

As regards the change of refractive index n with pressure p, experimental data are not so numerous for liquids; at least not in a form suitable for the present analysis, for which observations are needed at various wave-lengths. In order to illustrate the alternative formula (12), a set of observations on carbon disulphide is taken from a paper by Röntgen and Zehnder.* The data are the values of dn/dp for the B, D, and F lines, the compressibility $\beta = 89{\cdot}5\times10^{-6}$, and the index $n = 1{\cdot}6297$ for the sodium line. From the values for the sodium line we calculate the value of C in relation (12) and obtain thus

$$10^6\frac{dn}{dp} = 89{\cdot}5\,\frac{n^2-1}{2n}+22\,\frac{(n^2-1)^2}{2n}. \tag{16}$$

Estimating the values of n for the other two lines we can calculate from this equation the values of dn/dp. The results are shown in the following Table V:—

Table V.—Carbon Disulphide.

λ.	$10^6\frac{dn}{dp}$, obs.	$10^6\frac{dn}{dp}$, calc.
687	62·2	62·1
589	63·9	63·9
486	67·4	66·7

7. *Artificial Double Refraction in Liquids.*

In previous papers† the present scheme was developed in a simple form in connection with artificial double refraction produced by mechanical strain or by the action of an electric or magnetic field. The formal basis of the theory is the supposition that the effects can be represented by an œolotropic change in the quantity σ. If the density remains constant and if the medium becomes doubly refracting like a uniaxal crystal with n_1 and n_2 for principal refractive indices, the relation (10) becomes

---

* W. C. Röntgen and L. Zehnder, 'Annalen der Physik,' 1891, vol. 44, p. 24.

† 'Roy. Soc. Proc.,' A, vol. 80, p. 28, 1907; also 'Phys. Rev.,' 1909, vol. 28, p. 136.

$$\frac{1}{n_1^2-1}-\frac{1}{n_2^2-1} = \text{constant.} \tag{17}$$

If the changes are small, with n the refractive index for the isotropic medium at same density, we have

$$\frac{n\,dn}{(n^2-1)^2} = \text{constant.} \tag{18}$$

This relation has been confirmed by recent researches, at least as a first approximation for the double refraction induced in liquids by an electric or magnetic field; reference may be made to the experimental and theoretical investigations of McComb,* Skinner,† Cotton and Mouton,‡ and Natanson.§

Although the present aim is rather to include various phenomena within a single formal scheme than to analyse in detail the physical mechanism of each effect, a few remarks may be made in the present instance. All the relations such as (10), (17), and (18) have been developed by considering the medium as effectively an assemblage of optically isotropic particles; all the changes which occur in the dispersion, whether isotropic or œolotropic, are expressed in terms of two variables: the density ρ and the quantity σ. In the previous work quoted above the physical process was conceived of as a rearrangement of the particles in space. Cotton and Mouton prefer to regard it as an orientation of anisotropic molecules, and they give a theoretical deduction of relations (17) and (18) which is said to rest on this hypothesis.‖ Now this assumption is possibly preferable for certain physical reasons, but it is not clear where it enters into the proof referred to above. In fact the proof is formally the same as ours, in that it ascribes the birefraction to a directional variation in the quantity σ; the hypothesis of orientation enters in the assertion that it is the cause of these changes in σ, and of course if the particles are to orientate under a field of force they must be in some way anisotropic. Perhaps one might reconcile the hypothesis of orientation and the theoretical proof of relation (17) by considering the particles as in some way physically anisotropic but optically isotropic, just as one might regard for instance the particles of a crystalline substance which is optically isotropic; then one might have the possibility of orientation without interfering with the simplicity of isotropy in the optical equations.

---

* H. E. McComb, 'Phys. Rev.,' 1909, vol. 29, p. 525.

† C. Skinner, 'Phys. Rev.,' 1909, vol. 29, p 541.

‡ A. Cotton and H. Mouton, 'Ann. de Chim. et de Phys.,' 1910, vol. 19, p. 153.

§ L. Natanson, 'Bull. de l'Acad. des Sciences, Cracovie,' June, 1910.

‖ Cotton and Mouton, *loc. cit. ante*, p. 217.

If we wish to consider the particles as optically anisotropic, and the isotropy of the medium to be the result of averaging due to all possible orientations, we should have the following scheme. The equations of motion of a typical electron take, instead of (2), the form

$$\begin{aligned} m\frac{d^2x}{dt^2}+f_x x &= e(X+\alpha P_x), \\ m\frac{d^2y}{dt^2}+f_y y &= e(Y+\beta P_y), \\ m\frac{d^2z}{dt^2}+f_z z &= e(Z+\gamma P_z). \end{aligned} \tag{19}$$

Suppose now the extreme case when all the particles are orientated the same way; then we should have a crystalline medium with three principal refractive indices n_1, n_2, and n_3 given by the equations

$$\begin{aligned} \left(\sigma_1+\frac{1}{n_1^2-1}\right)^{-1} &= \Sigma\frac{C_{n1}}{\lambda^2-\lambda_{n1}^2}, \\ \left(\sigma_2+\frac{1}{n_2^2-1}\right)^{-1} &= \Sigma\frac{C_{n2}}{\lambda^2-\lambda_{n2}^2}, \\ \left(\sigma_3+\frac{1}{n_3^2-1}\right)^{-1} &= \Sigma\frac{C_{n3}}{\lambda^2-\lambda_{n3}^2}. \end{aligned} \tag{20}$$

On the other hand, if the particles are arranged at random in all possible directions, we should have an isotropic medium of index n_0, for which we could write

$$\left(\sigma_0+\frac{1}{n_0^2-1}\right)^{-1} = \Sigma\frac{C_n}{\lambda^2-\lambda_n^2}. \tag{21}$$

In general, if we admit optical anisotropy of the particles, this in itself would contribute directly to the observed double refraction, as well as indirectly through the alteration in the σ-quantities.

One hypothesis would be to ignore the quantities σ, or make them all equal; this would ascribe the doubly-refracting properties to the differences between λ_n, λ_{n1}, λ_{n2}, and λ_{n3}. But the relation between these quantities does not seem obvious, except that the right-hand side of (21) is in some way an average of those in (20).

Another hypothesis, one by which the simple relations (17) and (18) are obtained, is to regard the right-hand sides of equations (20) and (21) as all the same function of the wave-length λ; that is, we do, in effect, treat the molecules as if they were *optically* isotropic.

Cotton and Mouton have also investigated the variation of the induced double refraction with the temperature; they find that in general the diminution is greater with increase of temperature than could be accounted for by the mere change of density. This result was involved in one case in the calculation given by the present writer for carbon disulphide;* expressing the results of Blackwell in the form

$$dn = \mathrm{C}\frac{(n^2-1)^2}{n},$$

it was found that $\mathrm{C} = 4{\cdot}36 \times 10^{-7}$ at 11° and $\mathrm{C} = 4{\cdot}26 \times 10^{-7}$ at 24°.

So that, although the change in n is allowed for, there is in addition a decrease in C. With the present notation C is $\frac{1}{2}d\sigma$, and if we take the average decrease between the two temperatures we have

$$d(d\sigma)/dt = -1{\cdot}55 \times 10^{-9}.$$

It might be possible to connect this with the rate of change of σ with the temperature for the isotropic medium; but it would doubtless be necessary to examine in more detail the physical nature of the changes which occur.

[Since the above remarks were written, a preliminary note has been published by Langevin,† dealing with the theory of electric and magnetic double refraction from the point of view of molecular orientation; the note records the results obtained. Apparently the molecule is supposed to be anisotropic, but account is taken of differences between electric, magnetic, and optical asymmetry; the action of the external field is to modify the distribution of the molecular axes in space. As regards the dispersion, it is stated that the relation (18) above is obtained under certain conditions.]

8. *Temperature Variation in Solids.*

Although one expects more complexity in the case of solid substances, it seems of interest to express the experimental results by the same method as for liquids. It has been well established that the effect of temperature on the dispersion of solids is not merely due to the change of density, and it is here especially that recourse has been had to dispersion formulæ showing changes in the natural resonance-frequencies.

Glass.—The extensive researches of Pulfrich‡ are available, and we choose three examples which have already been examined by Voigt. The following Table VI shows the results:—

---

* *Loc. cit. ante*, p. 35.

† P. Langevin, 'Comptes Rendus,' August 16, 1910.

‡ C. Pulfrich, 'Annalen der Physik,' 1892, vol. 45, p. 609.

Table VI.

λ	656	589	486	434
S 57. Heavy Flint Glass, $\alpha = 2{\cdot}804 \times 10^{-5}$.				
n	1·9491	1·9625	1·9979	2·0303
$10^5\,dn$	1·204	1·447	2·090	2·810
T	−4·471	−4·876	−5·976	−7·190
10^5 C	1·60	1·68	1·86	2·07
O 527. Light Flint Glass, $\alpha = 2{\cdot}696 \times 10^{-5}$.				
n	1·5389	1·5718	1·6529	1·7187
$10^5\,dn$	−0·008	+0·014	+0·080	+0·137
T	−1·359	−1·488	−1·831	−2·127
10^5 C	1·95	1·85	1·64	1·50
S 40. Crown Glass, $\alpha = 2{\cdot}613 \times 10^{-5}$.				
n	1·5366	1·5619	1·6211	1·6680
$10^5\,dn$	−0·314	−0·305	−0·246	−0·237
T	−0·992	−1·075	−1·323	−1·505
10^5 C	1·40	1·35	1·30	1·22

In the above table, T is the quantity calculated by Voigt in the manner referred to previously (§3); for small changes the relation is

$$T = -\frac{2n}{\alpha}\,dn-(n^2-1),$$

where α is the cubical coefficient of expansion.

Also the quantity C of the present theory is given by

$$C = \frac{2n\,dn}{(n^2-1)^2}+\frac{\alpha}{n^2-1} = -\frac{\alpha}{(n^2-1)^2}\,T.$$

It appears that T is negative and increases numerically with decreasing wave-length. For the heavy glass S 57, the increase in the factor $(n^2-1)^2$ is not sufficient to counteract the increase in T, and the quantity C shows a regular increase; in the other two glasses the effect is the other way and C shows a regular decrease in the same direction.

One must remember that glass is not a simple substance but is a complex mixture, a fact which is illustrated by its optical behaviour under mechanical stress. Further, Pulfrich considered that the observed changes in refractive index were connected with a variation of absorption in the ultra-violet region; Königsberger* has also observed in solid bodies a displacement of this absorption region towards the longer wave-lengths with rising temperature. The direct influence of absorption has not been taken into account in the present theory, so that one cannot say how the results would be modified thereby.

---

* J. Königsberger, 'Annalen der Physik,' 1901, vol. 4, p. 796.

Meantime, it appears that the variation of the σ-quantity must play a considerable part in a complete theory of the phenomena. Similar general remarks apply to the following calculations, which are tabulated here for comparison.

Amorphous Quartz.—Observations on this substance have been made by Martens;[*] the wave-lengths range from 0·185 μ to 0·508 μ. With the usual notation the following Table VII shows the results for some of the wave-lengths. If the substance were the same as fused quartz or silica it would have a very small coefficient of expansion; whether this was the case or not, it appears that if we take α to have the mean value for quartz (0·000036), the values of C show a remarkable constancy in this range. If we calculate the values of T as before, we find it varies regularly from $-1·969$ at 508 $\mu\mu$ to $-3·510$ at 185 $\mu\mu$. We notice that dn/dt is positive in this range. If we take the mean value of C to be 55×10^{-6}, and if we assume C to remain constant, we can calculate when dn/dt would become negative; it would be zero when $n^2-1 = \alpha/C$, that is, when $n = 1·287$ approximately. As n is 1·575 at 185 $\mu\mu$ and 1·457 at 656 $\mu\mu$, the wave-length in question would be large; judging from the refractive index of ordinary quartz, it might be in the neighbourhood of 5 μ or 6 μ, approaching a region of absorption in the infra-red.

Table VII.—Amorphous Quartz.

λ.	$10^5 \frac{dn}{dt}$.	10^6 C.	λ.	$10^5 \frac{dn}{dt}$.	10^6 C.
185	2·319	57·6	298	1·225	54·2
193	2·080	56·5	346	1·141	54·4
206	1·832	55·7	361	1·127	54·6
214	1·728	55·5	441	1·041	54·4
226	1·590	55·0	480	1·020	54·3
257	1·374	54·4	508	1·021	54·7
274	1·301	54·3			

Fluor Spar and Rock Salt.—Micheli[†] has observed the variation of dn/dt for several substances, with wave-lengths ranging from about 185 $\mu\mu$ to 589 $\mu\mu$.

---

[*] F. F. Martens, 'Berichte der Deutsch. Phys. Ges.,' 1904, p. 308.

[†] F. J. Micheli, 'Annalen der Physik,' 1902, vol. 7, p. 772.

All the curves obtained by graphing dn/dt against λ show a rise towards smaller values of λ. The most striking result is that for rock salt, where dn/dt varies from $+2{\cdot}987$ at 202 $\mu\mu$ to $-3{\cdot}747$ at 643 $\mu\mu$. If we calculate the quantity C in this case, we find that it varies only slowly in the visible region, having a value of about 28×10^{-6}, but increases rapidly in the ultra-violet. If we use the value 28×10^{-6} to calculate where dn/dt changes sign, and estimate the wave-length from a dispersion formula, we obtain the position as 175 $\mu\mu$; the experimental curve cuts the axis at about 220 $\mu\mu$. Similar remarks apply to the calculations for fluor spar, where C has a value of about 24×10^{-6} in the visible region, but rises rapidly in the ultra-violet to 37×10^{-6} at 185 $\mu\mu$.

In the case of solids such as those examined above, we find that if we use the value of C in the visible region to calculate a curve for dn/dt, the curve so obtained falls below the experimental curve when the latter begins to vary rapidly in the ultra-violet.

It is unnecessary to add further calculations of the same type, or one might examine data available from experiments on elastic deformation of solids, or from the double refraction of natural crystals and its variation with temperature and pressure—probably with similar results. The general conclusion is that the variation of the quantity σ needs to be considered in each case, but the changes in solids are too complex to be brought under a simple scheme with only two or three variables.

9. *Change from Vapour to Liquid.*

In this region the relation $(n^2-1)/(n^2+2)\rho$ has had its greatest success compared with the other simple formulæ. Calculations for many substances have been given by Brühl;* from his data we calculate the quantity C the present theory for six typical substances, including those for which the Lorentz formula shows most disagreement. Two wave-lengths are given, the Li and Na lines; the data for the vapours are for a temperature of about 100°, while the liquids vary between 10° and 20°. Table VIII shows the values of C, the differences between values of $\rho/(n^2-1)$ for vapour and liquid, for the two wave-lengths; the agreement between the second and third columns is as good as could be expected. The values of $\frac{1}{3}(\rho_l-\rho_v)$ are given for comparison.

---

* Brühl, 'Zeitschrift für Phys. Chem.,' 1891, vol. 7, p. 1.

Table VIII.—Values of $C_{\text{liquid}}^{\text{vapour}}$.

λ	Li.	Na.	$\frac{1}{3}(\rho_l-\rho_v)$.	σ_l.
Carbon disulphide	0·3911	0·3907	0·4200	0·3094
Chloroform	0·4942	0·4952	0·5015	0·3276
Ethyl alcohol	0·2564	0·2565	0·2653	0·3214
Methyl alcohol	0·2671	0·2685	0·2645	0·3367
Propyl iodide	0·7524	0·7521	0·5775	0·4323
Benzene	0·3196	0·3209	0·2922	0·3639

10. *Absolute Values of* σ.

We have so far been concerned only with a difference equation, the quantity C_2^1 being equal to $\rho_2\sigma_2-\rho_1\sigma_1$; thus we obtain a relation between the values of σ in two different states. If we wish to assign numerical values to σ, we must fix its value in some standard state. At first it might be thought advisable to follow the ordinary theory, and make σ equal to $\frac{1}{3}$ in the gaseous state. If we try this for carbon disulphide we can calculate from Table VIII the value of σ for liquid CS_2 at 10°: knowing the densities of the vapour and liquid, and putting $C_l^v = 0{\cdot}391$, we obtain thus $\sigma_l = 0{\cdot}3104$. This is less than the value of σ in the gaseous state; but σ represents the additional force on a particle due to the surrounding molecules, so it seems preferable that σ should be greater for a substance in the liquid state than when gaseous. This result can be obtained by making σ very small for gases; this is allowable, as, owing to the small values of $n-1$, there is no evidence to decide between the degree of constancy of the various forms $(n-1)/\rho$, $(n^2-1)/\rho$ or $(n^2-1)/(n^2+2)\rho$.

To make the matter definite, we may decide provisionally to make σ zero for gases, and for simplicity we fix the standard state as the gaseous condition supposed to be at 0° and a pressure of 760 mm. With this assumption, the values of σ in the last column of Table VIII have been calculated. One cannot deduce much from the values, as the data for gases are possibly not very accurate and the liquids are at various temperatures; otherwise it might be of interest to trace, for instance, a connection between the values of σ and the chemical constitution of the substance. It may be noticed that the "specific refraction" is $1/\{\sigma+1/(n^2-1)\}\rho$; thus, for example, the large value of σ for propyl iodide would give a corresponding divergence in the specific refraction ordinarily used. On the present scheme, anomalies in molecular refraction might be ascribed, in part, at least, to the indirect effect of intra-molecular action specified by the σ-quantity.

Air.—Magri* has made observations on the refractive index of air at high densities; he found that $(n^2-1)/(n^2+2)\rho$ gave the best approach to constancy. In Table IX some of his results have been used to calculate σ; in the column under σ_0 are the values under the assumption that σ is zero in the standard state, while under $\sigma_{\frac{1}{3}}$ are the values if σ is $\frac{1}{3}$ in that state. The column $\frac{1}{3}(1-\rho_0/\rho)$ shows the value which σ should have in each case in order that $(n^2-1)/(n^2+2)\rho$ should have always its value for unit density; the last column gives the actual value of this quantity referred to unit density at 0° C. The temperature for the first row is 0° C, while for the other cases it varies between 14°·3 and 14°·9. Assuming the experimental data to be sufficiently acucrate, the variations both in σ and σ_0 are curious, σ_0 rising to a minimum with increasing density, and then falling to approximately $\frac{1}{3}$. It may be noticed how an apparently large difference between σ_0 and $\frac{1}{3}(1-\rho_0/\rho)$ makes little change in the values in the last column. The results given here are referred to later in § 12.

Table IX.—Air.

Density.	σ_0.	$\sigma_{\frac{1}{3}}$.	$\frac{1}{3}\left(1-\frac{\rho_0}{\rho}\right)$.	$\frac{n^2-1}{(n^2+2)\rho}\,10^7$.
1	0	0·3333	0	1953
14·84	0·004	0·0224	0·3109	1947
42·13	0·4715	0·4794	0·3254	1959
69·24	0·4363	0·4411	0·3285	1961
96·16	0·4030	0·4065	0·3299	1961
123·04	0·3549	0·3576	0·3306	1956
149·53	0·3495	0·3517	0·3311	1956
176·27	0·3352	0·3371	0·3314	1953

Carbon Disulphide.—By combining the observations of Flatow, referred to previously, with values of n for the vapour, we can see how the value of σ varies with temperature and density. For the vapour, we know n for one wave-length of the series used for the liquid, viz., the line 589 $\mu\mu$. If we use the data $\rho = 0{\cdot}00342$, $n = 1{\cdot}00148$, and $\sigma = 0$ for the vapour, together with $\rho = 1{\cdot}2931$ and $n = 1{\cdot}64411$ for the liquid at 0°, we find

---

* L. Magri, 'Physikalische Zeitschrift,' 1905, vol. 6, p. 629.

$\sigma = 0{\cdot}3069$. Using this value for all wave-lengths at 0°, we can calculate the values for various wave-lengths at 20° and 40°; the results for four cases are contained in Table X. There is a small regular increase in σ with rise in temperature, although the density diminishes.

Table X.—Values of σ for CS_2; $\sigma_0 = 0{\cdot}3069$.

λ.	20°.	40°.
274	0·3087	0·3112
441	0·3094	0·3117
508	0·3093	0·3119
589	0·3092	0·3118
Mean ……	0·3091	0·3116

Water.—For the vapour we use $\rho = 0{\cdot}000809$, $\sigma = 0$, and $n = 1{\cdot}00025$ for sodium light. Carrying out similar calculations, we find the following series of mean values of σ for the liquid:—

0°.	20°.	40°.	60°.	80°.
0·3362	0·3350	0·3344	0·33361	0·33364

It is of interest to compare with these some values for ice, which is a uniaxal crystal; Pulfrich has measured the two indices n_0 and n_e for various wave-lengths. Let σ_0 and σ_e be the corresponding principal values of σ for ice at 0°; with the density $\rho' = 0{\cdot}91674$, the following table shows the values of $\rho'/(n_0^2-1)-\rho'/(n_e^2-1)$ for certain wave-lengths, using absolute values of the indices:—

Ice.

λ………	760	670	589	485
C_e^0 ………	0·00625	0·00632	0·00608	0·00628

Now for water at 0°, and at wave-length 589, we have $\rho/(n^2-1) = 1{\cdot}28174$; thus, if σ_w is the value for water at 0°, we have the equations

$$\rho'(\sigma_e-\sigma_0) = 0{\cdot}00608 = C_e^0,$$
$$\rho\sigma_w-\rho'\sigma_0 = 0{\cdot}00079 = C_w^0,$$
$$\rho'\sigma_e-\rho\sigma_w = 0{\cdot}00529 = C_e^w,$$

From these, with $\sigma_w = 0{\cdot}3362$, we find $\sigma_0 = 0{\cdot}3660$ and $\sigma_e = 0{\cdot}3726$. The actual numbers would probably be modified with more information with which to compare them; however, it appears that in the change to the solid state σ is increased.

11. *Dispersion Formulæ: Absorption Maxima.*

It would seem possible to obtain values of σ by constructing dispersion formulæ of a suitable type; before examining a few cases it is necessary to consider certain points in regard to the wave-lengths for which absorption is a maximum. The argument may be given first for a simple formula, such as

$$n^2-1 = \Sigma_s \frac{C_s}{\lambda^2-\lambda_s^2}. \tag{22}$$

Consider the values of n in the neighbourhood of a "resonance" wave-length, say λ_1; suppose that this is sufficiently isolated so that we may take the other terms in (22) as constant, that is, we write

$$n^2 = q_1 + \frac{C_1}{\lambda^2-\lambda_1^2}. \tag{23}$$

From this equation n^2 is negative, and consequently n imaginary, for the range of wave-length given by $(\lambda_1^2-c_1/q_1)^{\frac{1}{2}} < \lambda < \lambda_1$. If in (23) we regard n as complex and equal to $n(1-i\kappa)$ we should have $n\kappa$ zero, except within the above range, where it increases from zero at the lower limit to infinity at the upper limit λ_1. This effect is, of course, not a true absorption effect, but would mean that the medium refused to admit certain radiation within a definite range of wave-length. If we now insert a term in the equations of the medium to represent absorption, we have instead of (23), an equation

$$n^2(1-i\kappa)^2 = q_1 + \frac{C_1}{\lambda^2-\lambda_1^2+ib_1\lambda}. \tag{24}$$

Following the method used by Lorentz* for a similar equation with q_1 equal to unity, we write the last term of (24) as $c_1/(\alpha+i\beta)$; then we have

$$n^2(1-\kappa^2) = q_1 + \frac{C_1\alpha}{\alpha^2+\beta^2}; \qquad 2n^2\kappa = \frac{C_1\beta}{\alpha^2+\beta^2}. \tag{25}$$

Solving these, we obtain

$$2n^2 = \sqrt{q_1^2+\frac{C_1^2+2q_1C_1\alpha}{\alpha^2+\beta^2}} + q_1 + \frac{C_1\alpha}{\alpha^2+\beta^2},$$

$$2n^2\kappa^2 = \sqrt{q_1^2+\frac{C_1^2+2q_1C_1\alpha}{\alpha^2+\beta^2}} - q_1 - \frac{C_1\alpha}{\alpha^2+\beta^2}. \tag{26}$$

If we assume, further, the usual simplification, viz., that β is large, we obtain finally the approximate result

$$n\kappa = \frac{C_1\beta}{2q_1^{\frac{1}{2}}(\alpha^2+\beta^2)}. \tag{27}$$

---

* H. A. Lorentz, 'The Theory of Electrons,' p. 310.

Thus the retention of q_1 does not affect the form of the result, and the deduction follows that the maximum of $n\kappa$ is in the neighbourhood of $\alpha = 0$, that is, of the wave-length λ_1.

Returning to the dispersion formula (22), the previous argument is of the type which has been relied on when the quantities λ_s have been identified with absorption maxima observed experimentally; as far as the simple formula is concerned, these quantities are the upper limits of the ranges in which n is imaginary and are the wave-lengths for which n^2 is infinite.

If we turn now to the type of formula used in the previous work, we have

$$\frac{1}{\sigma+1/(n^2-1)}\frac{1}{\rho} = \Sigma\frac{C_s}{\lambda^2-\lambda_s{}^2}. \tag{28}$$

In the neighbourhood of λ_1 we have now

$$\frac{1}{\sigma+1/(n^2-1)}\frac{1}{\rho} = q_1+\frac{C_1}{\lambda^2-\lambda_1{}^2}. \tag{29}$$

If we solve this for n^2 we find

$$n^2 = q_1{}'+\frac{C_1{}'}{\lambda^2-\lambda_1{}'^2}, \tag{30}$$

with $$q_1{}' = \frac{1+q_1\rho(1-\sigma)}{1-q_1\rho\sigma}; \qquad C_1{}' = \frac{C_1\rho}{(1-q_1\rho\sigma)^2};$$

$$\lambda_1{}'^2 = \lambda_1{}^2+\frac{C_1\rho\sigma}{1-q_1\rho\sigma}.$$

The lower limit for which n is imaginary is equal to

$$\sqrt{(\lambda_1{}'^2-C_1{}'/q_1{}')} = \left\{\lambda_1{}^2-\frac{C_1\rho\,(1-\sigma)}{1+q_1\rho\,(1-\sigma)}\right\}^{\frac{1}{2}},$$

while the upper limit is

$$\lambda_1{}' = \left\{\lambda_1{}^2+\frac{C_1\rho\sigma}{1-q_1\rho\sigma}\right\}^{\frac{1}{2}}. \tag{31}$$

Thus both the limits of the range of imaginary values for n are altered by the introduction of the quantity σ, a fact which was noticed by Larmor* in discussing optical dispersion. It is clear that if we introduce a term representing true absorption, the argument would follow the same lines from equation (30) as from equation (23); consequently, we are led to identify the absorption maximum with the upper limit of the above range in (31). With a dispersion formula of type (28), the quantities λ_s represent true "resonance" wave-lengths belonging to the individual atom or molecule; it is not permissible to identify them with maxima of absorption, or selective reflection, which have been determined experimentally for the medium as a whole. To determine the latter, in any case, we must write the dispersion formula as in (29), and the wave-length required is $\{\lambda_1^2+C_1\rho\sigma/(1-q_1\rho\sigma)\}^{\frac{1}{2}}$, instead of λ_1.

---

* J. Larmor, 'Phil. Trans.,' A, 1897, vol. 190, p. 240.

Numerical illustrations may be taken from two cases, where a dispersion formula of the type (28) has been used without taking account of this change.

Carbon Disulphide.—In the paper already quoted, Flatow has calculated dispersion formulæ of the type

$$n^2 = m+\frac{m'\lambda^2}{\lambda^2-\lambda'^2}-k\lambda^2$$

for CS_2 at various temperatures; he finds λ' to be about 0·227 μ, varying slightly with the temperature. There is a region of absorption ranging from 0·190 μ to 0·228 μ with a maximum at 0·210 μ approximately; there is also a minor region of absorption near 0·325 μ. By a method of continued reflection, Flatow found a maximum at 0·231 μ and concludes that the value of 0·227 μ for λ' agrees well with this for a natural frequency. He also states that a dispersion formula of the Lorentz-Planck type gives a value of 0·185μ for λ', and consequently gives a worse agreement than the older form. In the latter calculation Flatow ignores the effect considered above, and also uses a specially simple type of formula, viz. $(n^2-1)/(n^2+2) = g\lambda^2/(\lambda^2-\lambda'^2)$. But for carbon disulphide we must use at least a three-constant formula. Suppose, for comparison, we assume that σ is $\frac{1}{3}$, and make the calculations with

$$\frac{n^2-1}{n^2+2} = q+\frac{C_1}{\lambda^2-\lambda_1^2}$$

determining the constants from the data

λ	441	508	589
n	1·67180	1·64586	1·62806

With sufficient approximation for the purpose we find the values

$$q = 0{\cdot}33567, \qquad C_1 = 0{\cdot}005843, \qquad \lambda_1^2 = 0{\cdot}04338.$$

Thus we find λ' is 0·208 μ. But this is not to be compared with the experimental data; according to the previous argument, the quantity to be so used is $\sqrt{\{\lambda_1^2+C_1/(1-q)\}}$ in the present notation. Working this out for the above values we find the value 0·228 μ, giving practically the same agreement as the older formula.

Rock Salt and Fluorite.—Following Larmor's development of the present type of dispersion formula, to which reference was made above, Maclaurin* has deduced and illustrated the form

$$\frac{n^2-1}{n^2+a} = \Sigma\frac{C_s}{\lambda^2-\lambda_s^2}. \qquad (32)$$

---

* R. C. Maclaurin, 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 367.

For a given physical state of the medium this form is equivalent to (28) above, with a equal to $(1-\sigma)/\sigma$; however, the previous form is preferable when we wish to consider changes of dispersion for changing physical conditions, and it also enables us to separate out a quantity independent of these conditions.

Maclaurin gives numerical calculations for two substances, rock salt and fluorite; identifying $n(\infty)$ with the dielectric constant K, he uses (32) in the form

$$\frac{n^2-1}{n^2+a} = \frac{\mathrm{K}-1}{\mathrm{K}+a} + \frac{\mathrm{C}_1}{\lambda^2-\lambda_1{}^2} + \frac{\mathrm{C}_2}{\lambda^2-\lambda_2{}^2}. \tag{33}$$

A very close agreement is shown between calculated and observed values of n over a large range of wave-length; in addition Maclaurin claims that K, λ_1, and λ_2 agree with the mean values of the best experimental data. However, the quantities λ_1 and λ_2 are identified directly with the observed maxima of absorption or reflexion; we calculate now what difference is made by the argument of the present section, using Maclaurin's values of the constants for the dispersion formula (33).

For rock salt we have—

$\lambda_1{}^2 = 0{\cdot}0160074,$ $\quad\lambda_2{}^2 = 2632{\cdot}14,$

$\mathrm{C}_1 = 0{\cdot}00191605,$ $\quad\mathrm{C}_2 = 683{\cdot}816,$

$a = 5{\cdot}51,$ $\quad\mathrm{K} = 5{\cdot}9,$

$\lambda_1 = 0{\cdot}12652\,\mu,$ $\quad\lambda_2 = 51{\cdot}3\,\mu.$

Putting λ_1 for λ in the last term of (33), we have, in the vicinity of λ_1,

$$\frac{n^2-1}{n^2+5{\cdot}51} = q' + \frac{\mathrm{C}_1}{\lambda^2-\lambda_1{}^2}, \quad \text{with} \quad q' = 0{\cdot}169652.$$

Hence the required wave-length is given by $\sqrt{\{\lambda_1{}^2+\mathrm{C}_1/(1-q')\}}$, that is, $0{\cdot}1353\,\mu$. The lower limit of the range for which n is imaginary is $\sqrt{\{\lambda_1{}^2-a\mathrm{C}_1/(1+aq')\}}$ or $0{\cdot}1027\,\mu$. We have seen that it is the upper limit which, consistently with the similar argument for the simpler dispersion formula, should be identified with the experimental data.

For the neighbourhood of λ_2 we find $q'=0{\cdot}429449$ and the result is that n is imaginary between $38{\cdot}9\,\mu$ and $61{\cdot}9\,\mu$; hence if we use the numerical values given above it is $61{\cdot}9\,\mu$ that should be compared with experiment instead of $51{\cdot}3\,\mu$.

We may compare with this Paschen's formula for rock salt of the Sellmeier type;* this gives a natural wave-length of $60\,\mu$ in the infra-red and in its neighbourhood we have $n^2=5{\cdot}680142+12059{\cdot}95/(\lambda^2-3600)$. We find then that n is imaginary between approximately $38{\cdot}4\,\mu$ and $60\,\mu$; the upper limit

---

[*] F. Paschen, 'Annalen der Physik,' 1908, vol. 26, p. 130.

being compared with the absorption maximum, although Paschen regards it as an open question how far the observed "Reststralhen" maxima can be identified with the wave-lengths of the natural vibrations which dominate the dispersion in the infra-red.

A smaller value of the constant a would probably give a better agreement in this respect. In fact Maclaurin states that he tried at first a equal to 2; he found then a fair agreement between calculated and observed values of n, but with the values of λ_1 and λ_2 as much below the observed values as they were above them with an ordinary Sellmeier dispersion formula.

As regards dispersion formulæ in general, it should be remembered that we replace the actual substance by an ideal simplified medium with only two or three natural frequencies; it may happen that the actual substance has two or three very predominant regions of resonance, in which case there should be good agreement between calculated and observed positions for these. On the other hand it may be that there are two or three regions of equal value not far apart, and the calculated value would be a mean position. For instance, recent observations on rock salt show maxima at 46·9 μ and 53·6 μ.* It appears that the quality of the agreement between observed and calculated values of refractive index even over a considerable range is not sufficient in itself to decide between different hypotheses, and for instance to give reliable values of a or σ.

In respect to the absorption regions in the infra-red, the dispersion often gives no more than a single term $-k\lambda^2$, which we could make up from any number of places of selective absorption in the absence of further information; numerical values are obtained only when we assume the definite simplification of a small number of natural frequencies and use the value of the dielectric constant.

For fluorite Maclaurin gives the following values :—

$$\begin{aligned} \lambda_1^2 &= 0·00716764, & \lambda_2^2 &= 576·353, \\ C_1 &= 0·001303, & C_2 &= 231·856, \\ a &= 1·04, & K &= 6·8, \\ \lambda_1 &= 0·0846618\,\mu, & \lambda_2 &= 24·0074\,\mu. \end{aligned}$$

With the same notation as before, we find in the neighbourhood of λ_1 that $q' = 0·337497$; hence $\surd\{\lambda_1^2+C_1/(1-q')\} = 0·09557\ \mu$. Also near λ_2 we have $q' = 0·739785$, and $\surd\{\lambda_2^2+C_2/(1-q')\} = 38·3\ \mu$. The relative displacements are larger here owing to the larger values of q' than in the former case.

If we used the value of a obtained from these formulæ we could calculate

---

* Rubens and Hollnagel, 'Sitzungsber.,' Berlin, 1910.

σ equal to $1/(1+a)$; this would give for rock salt $\sigma = 0{\cdot}15$, and for fluorite $\sigma = 0{\cdot}49$. But the preceding argument indicates that the calculations need considerable revision.

12. *Pressure and Temperature Displacement of Absorption Maxima.*

We shall consider now the displacement of absorption maxima under varying physical conditions, illustrating this by calculations for three cases in which suitable data are available.

Air.—The first example shows the effect of change of pressure and density in a gas, and we use Magri's experiments on air already examined in § 10. For a dispersion formula under ordinary standard conditions we have one obtained by C. and M. Cuthbertson* in the form

$$n-1 = \frac{4{\cdot}6463 \times 10^{27}}{16125 \times 10^{27} - p^2}, \tag{34}$$

where p is frequency. Using the density of air as $\rho_0 = 0{\cdot}00129$ we put this into a form suitable for present calculations and obtain

$$\frac{n^2-1}{\rho_0} = q + \frac{C_1}{\lambda^2 - \lambda_1{}^2}, \tag{35}$$

with $q = 0{\cdot}44674$; $C_1 = 0{\cdot}002493$; $\lambda_1{}^2 = 0{\cdot}0055814$; $\lambda_1 = 0{\cdot}074708\,\mu$. To make the calculations definite we assume, as in § 10, that σ is zero in the standard condition, so that the quantity on the right of (35) is invariant as regards physical conditions and depends only on the atomic or molecular constitution. In any other physical state the quantity on the left of (35) is altered so that we have then

$$\frac{1}{\sigma + 1/(n^2-1)} \frac{1}{\rho} = q + \frac{C_1}{\lambda^2 - \lambda_1{}^2}.$$

The argument of the previous section shows that the observed maximum of absorption in any condition should be near the wave-length λ' given by

$$\lambda' = \sqrt{\left\{\lambda_1{}^2 + \frac{C_1}{1/\rho\sigma - q}\right\}}. \tag{36}$$

We obtain the following series of values of λ' corresponding to the values of the relative density D :—

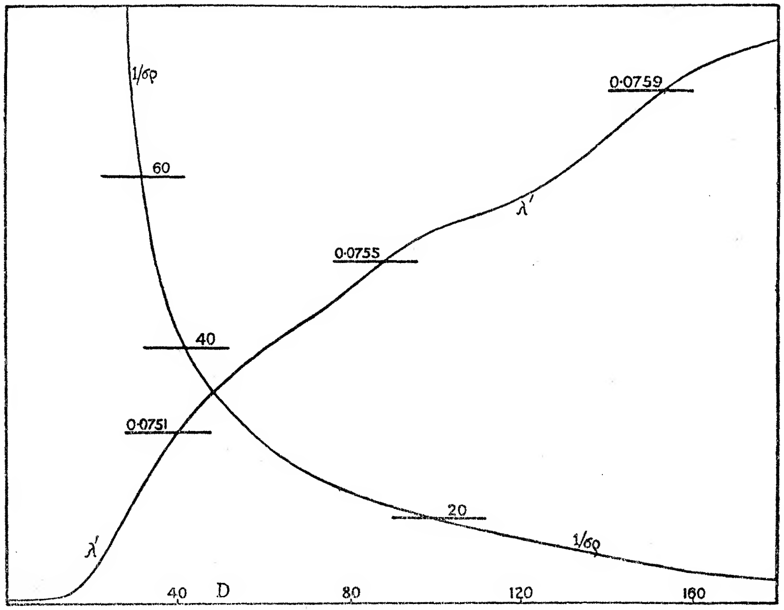
---

* C. and M. Cuthbertson, 'Roy. Soc. Proc.,' 1909, A, vol. 83, p. 170.

Table XI.—Air.

D.	λ′.	D.	λ′.
1	0·07471 −	69·24	0·07536
14·84	0·07471 +	123·04	0·07566
28·58	0·07494	149·53	0·07586
42·13	0·07514	176·27	0·07601

The curves in the figure show the variation of λ′ and of $1/\rho\sigma$ with the relative density D.



One may notice the slight initial increase of λ′, then a sharp rise between the values of 15 and 40 for D, followed by an approximately steady rise. We see also that $1/\sigma\rho$ decreases steadily with increasing density, falling sharply from an infinite value in the initial stages. No doubt the peculiarities at the lower values of D are due largely to the assumption that σ is zero initially. Still it does not seem possible to obliterate them entirely by assigning σ some small positive value initially; it is conceivable that there may be a stage at which the inter-molecular action specified by σ becomes suddenly appreciable. One may notice a possible analogy between the variation of λ′ in the present case and the pressure displacement of lines in an emission spectrum.

Carbon Disulphide.—We can make calculations for CS_2 with the observations of Flatow and the values of refractive index obtained by Rubens for longer wave-lengths. If we know n for a given wave-length for a physical state of the medium defined by ρ and σ, the quantity $\{\sigma+1/(n^2-1)\}\rho$ is independent of physical conditions; thus, by collecting observations at various temperatures, we can form an average set of values showing this molecular dispersion. With the convention adopted for assigning numerical values to σ, this would give, in fact, the values of $(n^2-1)/\rho$ for the substance as a gas at 0° and 760 mm. For reasons which have been indicated previously, it has not been thought advisable to try for a complete dispersion formula for this substance. However, four wave-lengths have been chosen, covering the range available, so as to form a four-constant formula to illustrate the present scheme. Using the values of σ given in §10 and the observations referred to above, we find

λ	0·274.	0·508.	1·037.	1·998.
Specific refraction	1·2368	0·8850	0·8274	0·8150

Before proceeding, we may notice the corresponding values of n for the vapour; using $\rho = 0{\cdot}00342$, we obtain for these four wave-lengths in order the values 1·002113, 1·001512, 1·001414, 1·001393. The values of σ were, of course, calculated with the help of the observed value of 1·00148 for the wave-length 0·589. The values of n so calculated would be values for the vapour, on the assumption that the change from liquid to vapour involves only physical changes which can be expressed optically in terms of ρ and σ; for instance, if some of the regions of absorption or resonance in the liquid were due entirely to molecular aggregates which were dissociated in the gaseous condition, then from this point of view the vapour would be optically a different substance. However, in most cases there does not appear to be an actual disappearance or creation of the principal dominating resonances, but only displacement and modification with changing conditions. We use the data above to determine the constants of a formula

$$\frac{1}{\sigma+1/(n^2-1)}\,\frac{1}{\rho} = q+\frac{C_1}{\lambda^2-\lambda_1^2}-k\lambda^2. \tag{37}$$

With sufficient approximation for our purpose, we find

$$q = 0{\cdot}8123,\quad C_1 = 0{\cdot}016077,\quad \lambda_1^2 = 0{\cdot}03721,\quad k = 0{\cdot}00036.$$

This gives a value of 0·1929 for λ_1. If we take the dielectric constant to be given by $K = 2{\cdot}6233-0{\cdot}00249\,(t-5^\circ)$ for liquid CS_2, we obtain a mean value of 0·8420 for the left-hand side of (37) for λ infinite; using this, we may replace the term $-k\lambda^2$ by a single equivalent absorption region in the infra-red. We obtain in this way a term $C_2/(\lambda^2-\lambda_2^2)$ with now $q = 0{\cdot}8420$, $C_2 = 2{\cdot}4502$, and $\lambda_2 = 9{\cdot}08\,\mu$. Experiment has shown that carbon disulphide has specially strong absorption in the region between $6{\cdot}6\,\mu$ and $10\,\mu$.* In any given state the maxima of absorption occur at wave-lengths λ_1' and λ_2', given, as in the previous sections, by expressions like $\{\lambda_1^2 + C_1/(1/\sigma\rho - q')\}^{\frac{1}{2}}$, when the dispersion formula has been put into a form suitable for the vicinity of the wave-length in question. Table XII shows the results for the gas and the liquid at three temperatures.

Table XII.—Carbon Disulphide.

	Liquid.			Gas.
	0°.	20°.	40°.	0°.
λ_1'	0·2159	0·2154	0·2149	0·1929
λ_2'	9·161	9·159	9·158	9·08

It is seen that λ' is displaced towards the shorter wave-lengths with increasing temperature. This appears to be the general rule for liquids, in contrast apparently to the behaviour of solids.

Water.—We examine now in the same manner Flatow's observations on water at five different temperatures; the values of σ were calculated in § 10, from a certain value of n for water vapour. Using these values we calculate the specific refraction for four wave-lengths; the following table shows the values at the various temperatures and the mean for each wave-length.

Table XIII.—Values of $1/\{\sigma + 1/(n^2-1)\}\,\rho$ for Water.

λ.	0°.	20°.	40°.	60°.	80°.	Mean.
274	0·67374	0·67368	0·67379	0·67409	0·67439	0·67394
361	0·64233	0·64225	0·64224	0·64229	0·64230	0·64228
480	0·62567	0·62571	0·62568	0·62566	0·62552	0·62565
589	0·61808	0·61815	0·61811	0·61803	0·61782	0·61804

Using the mean values and a density of 0·000809 for water vapour, with σ zero, we find the following values of n for these four wave-lengths in order: 1·000273, 1·000260, 1·000253, 1·000250; the last value is of course the one which was used in order to calculate the values of σ for the liquid.

---

* *Cf.* Winkelmann, 'Handbuch,' vol. 3, p. 350.

Using the mean values above, we calculate the constants of a dispersion formula of the type (37) and find

$$q = 0{\cdot}60961;\quad C_1 = 0{\cdot}003898;\quad \lambda_1^2 = 0{\cdot}015110;\quad k = 0{\cdot}00899.$$

The value of λ_1 is $0{\cdot}1229\ \mu$; we calculate now the values of λ_1' near which occur the maxima of selective absorption in the ultra-violet at the various temperatures. The following table shows the data and the results for the liquid, using $q' = 0{\cdot}60947$.

t	0°.	20°.	40°.	60°.	80°.
σ	0·33622	0·33497	0·33439	0·33361	0·33364
ρ	0·999874	0·998235	0·99233	0·98331	0·97191
λ_1'.........	0·1294	0·1293	0·1293	0·1292	0·1291

In the formula for λ_1' it is the product $\sigma\rho$ which occurs as the variable; this decreases continuously in this case and we find a corresponding regular but very slight decrease in λ_1' with rising temperature. This result is in contradiction with that deduced by Flatow; he calculated the constants of a Sellmeier dispersion formula for each temperature and found a fairly regular increase in λ_1 with rising temperature, the values ranging from $0{\cdot}126\ \mu$ to $0{\cdot}128\ \mu$ approximately. There is, of course, no direct experimental evidence available in this case. In general the experimental data for the variation of absorption maxima with temperature are rather conflicting in character; the results appear to depend on circumstances such as the homogeneity of the medium and the character, selective or general, of the absorption. It has been stated that in several cases, at least in the ultra-violet, the maxima are displaced towards the shorter wave-lengths with increase of temperature for liquids, while for solids they move to the longer wave-lengths.

If we wish to study the resonance in the infra-red we must replace the term $-k\lambda^2$ of the dispersion formula by the effect of one or more equivalent terms; we try first a single term $C_2/(\lambda_2 - \lambda_2^2)$. If we take for the calculation the values of the dielectric constant given by Ratz, namely 87·7 at 0° and 79·9 at 20°, and if we use the corresponding values of σ given above, we obtain a mean value of 2·8787 for the specific refraction for infinite wave-length; hence C_2 and λ_2 are given by $C_2/\lambda_2^2 = 2{\cdot}2691$; $C_2/\lambda_2^4 = 0{\cdot}00899$. These give the values $C_2 = 572{\cdot}7$ and $\lambda = 15{\cdot}88\ \mu$. If, with the same notation as before, we form λ_2' in order to find the approximate position of the absorption maximum, we find that λ_2' ranges from about $79\ \mu$ at 0° to $55\ \mu$ at 80°. This large variation is due to the large values of C_2 and q', and these come directly from the abnormal value of the dielectric constant; the only inference is that if we insist on bringing the dielectric constant in this case under the same scheme as the ordinary dispersion, one resonance in the infra-red is not sufficient. It is well known that Sellmeier dispersion formulæ with the same assumption indicate 76 μ as the approximate position, and the subject has been studied experimentally recently. Using ice, Trowbridge and Spence* find no metallic reflection between 45 μ and 82·3 μ; with water, Rubens and Hollnagel† obtain a similar result and also deduce that at 82·3 μ the refractive index is of the same order of magnitude as in the visible spectrum.

We may use this information in attempting to make up the term $-k\lambda^2$ from two resonance terms, $C_2/(\lambda^2-\lambda_2^2)+C_3/(\lambda^2-\lambda_3^2)$. To make the matter definite, we assume that n is 1·4 at 80 μ; then, with this and the above data for the dispersion, we have the equations

$$\frac{C_2}{\lambda_2^2}+\frac{C_3}{\lambda_3^2}=2{\cdot}269, \qquad \frac{C_2}{\lambda_2^4}+\frac{C_3}{\lambda_3^4}=0{\cdot}00899, \qquad \frac{C_2}{80^2-\lambda_2^2}+\frac{C_3}{80^2-\lambda_3^2}=-2{\cdot}13.$$

We have only three equations, with four unknown quantities; but to illustrate the calculations we assume a value for λ_2, say 10 μ. Then, solving the equations approximately, we find $C_2 = 89{\cdot}2$; $C_3 = 24676$; $\lambda_3 = 134\,\mu$. Calculating now, as before, the positions of selective absorption corresponding to λ_2 at the various temperatures, we find they range from 14·2 μ at 0° to 12·5 μ at 80°. The principal absorption corresponding to λ_3 is far removed in the infra-red; the results appear to be fairly consistent with the absorption of water, and they confirm at least the necessity for more than one selective absorption in the infra-red.

13. *Summary.*

The chief results of the previous investigation may be summarised briefly in the following manner:—

1. The formal scheme of the theory is the representation of the effect of the physical state of the medium upon its dispersion by means of two variables: the density ρ, and a quantity σ expressing an effect of surrounding molecules.

2. A relation independent of σ is deduced, and is used as a test of the theory, namely, the difference of $\rho/(n^2-1)$ for any two physical states is independent of the wave-length.

3. As the result of an analysis of available experimental data, it appears that the scheme is sufficiently adequate for gases, for liquids, and for changes of state from gas to liquid. For solid substances, the two variables ρ and σ

---

* A. Trowbridge and B. J. Spence, 'Phys. Rev.,' July, 1910.

† Rubens and Hollnagel, *loc. cit.*

are not sufficient to express all the facts, but it seems that the term involving σ must at least be taken into account in a complete theory.

4. It is shown that it is possible to include, either wholly or in part, the dispersion of artificial or natural double refraction in simple cases.

5. By assigning a standard state for the medium, gas at 0° and 760 mm., for which σ is zero, numerical values of σ are obtained for various substances in different states. Anomalies in molecular refractivity are ascribed, in part, to the variations in σ.

6. Using a type of dispersion formula involving ρ and σ, it is shown that the positions of the absorption maxima depend upon these quantities as well as upon the frequencies of the natural vibrations of the molecule. The consequent displacement of the maxima for varying conditions of pressure temperature, and density are illustrated by analysing certain experimental data.

The Spectrum of Halley's Comet.

By Charles P. Butler, A.R.C Sc., F.R.P.S., F.R.A.S.

(Communicated by Sir Norman Lockyer, K.C.B., F.R.S. Received November 5,—Read November 24, 1910.)

[Plate 7.]

Owing to the interference of high buildings it was impossible to arrange for observations of the comet spectrum during May from the Solar Physics Observatory at South Kensington. Sir Norman Lockyer therefore obtained permission to occupy the site on Fosterdown Fort, Caterham, which has already been selected as the future position of the Observatory.

No observations of value were possible during the first three weeks of May on account of exceptionally bad weather; but on May 23 and 26 photographs and visual observations of the spectrum were secured.

The spectrum was seen as a small nebulous cloud about 3′ to 5′ in diameter; with a binocular the central brightening due to the intense stellar nucleus became clearly visible. As a whole the comet was about as conspicuous as a second magnitude star, so that it was much fainter than had been expected. The curvature of the head was not so sharp as that seen in Comet 1910 *a*, giving the appearance of an elongated arc perpendicular to the tail extension when seen with moderate power.

Photographs of the comet were obtained with a Dallmeyer camera of